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Synthesis and structure of new diarene-bridged bi- and polymetallic compounds

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Abstract

Phenylcyclopentadiene (2) and diphenylcyclopentadiene (10) have been used to make bi- and polymetallic compounds. Compounds 2 and 10 have been used to make Cr–Fe bimetallic (5), Fe–Cr₂ trimetallic (6), Cr–Mn–Fe trimetallic (7), Fe–Mn₂ trimetallic (8), Mn–Cr bimetallic (12), Cr–Mn₂ trimetallic (13), Fe₂ bimetallic (15) and Fe–Cr₄ pentametallic (17) compounds. The molecular structures of 8 and 12 have been determined by X-ray crystallography.

Keywords: Diarene complexes; Polymetallic complexes; Crystal structures

1. Introduction

Cyclopentadienyl ligands are one of the most popular ligands in organometallic chemistry, and complexes of cyclopentadienyl ligands are known for all transition and most fblock metals [1]. Cyclopentadienyl ligands have been synthesized by various methods [2]. One of the strategies used to synthesize cyclopentadienyl metal compounds is the use of cyclopentenone as a starting material [3]. The Pauson–Khand reaction is one of the most effective methods in the syntheses of cyclopentenones [4]. Recently, we reported the preparation of 1,2-disubstituted or 1,2,3-trisubstituted cyclopentadienyl ligands from the Pauson–Khand reaction products [5], opening up a more general route to the preparation of various cyclopentadienyl ligands.

Substituted cyclopentadienyl complexes differ greatly from their unsubstituted counterparts in reactivity, structural features and physical properties [6]. As a result, many researchers have concentrated their efforts to synthesize highly substituted cyclopentadienyl ligands [7]. However, much less is known about the use of highly substituted cyclopentadienyl ligands to prepare bi- and polymetallic compounds. Recently, bimetallic compounds linked by pairs of cyclopentadienyl moieties, as in fulvalene [8], fluorene [9] and indenyl [10], have been reported. Vollhardt and coworkers [11] reported the synthesis and reactions of the terand quarter-cyclopentadienyls and their transition metal complexes. Ligands of these types will be able to hold several metals in close proximity, thereby allowing researchers to investigate whether cooperative effects can enhance or modify the chemical reactivity of metal complexes with regard to the mono-Cp analogs. This could result in new multimetal catalysts [12], organometallic polymers [13], heteropolymetallics [14], or redox active compounds [15].

Herein, we report the syntheses and structures of bi- and polymetallic compounds bridged by phenylcyclopentadienyl and 1,3-diphenylcyclopentadienyl ligands. The chemistry related to the use of phenylcyclopentadienylthallium has been previously reported by Rausch and co-workers [16]. However, they only reported cyclopentadienyl complexes.

2. Experimental

All reactions were conducted under nitrogen using standard Schlenk type flask and cannula techniques. Workup procedures were done in air.

Elemental analyses were done at the Chemical Analytic Center, College of Engineering, Seoul National University. ¹H NMR spectra were obtained with a Varian XL-200 instrument. IR spectra were recorded on a Shimadzu IR-470 (spectra measured as films on NaCl by evaporation of solvent). Mass spectra were recorded with a VG ZAB-E doublefocusing mass spectrometer.

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Compounds 1, 9, 10 and $[(naphthalene)Mn(CO)_3]BF_4$ were synthesized according to the published procedures [5,17,18]. Compound 10 was previously published [19].

2.1. Synthesis of 3

Compound **2** (0.66 g, 4.6 mmol) and Mn₂(CO)₁₀ (2.0 g, 5.1 mmol) were dissolved in 30 ml of xylene. The solution was refluxed for 2 days. After cooling to room temperature, the solvent was removed, and the residue was extracted with diethyl ether. The etheral solution was filtered through celite. The filtrate was concentrated and column chromatographed on silica gel eluting with hexane. After purification, bright yellow oil was obtained in 50% (0.64 g) yield. IR (NaC1): ν (CO) 2020, 1920 cm⁻¹. ¹H NMR (CDCl₃): δ 7.42–7.26 (m, 5H), 5.19 (t, 2.2 Hz, 2H), 4.78 (t, 2.2 Hz, 2H) ppm. HRMS: *M*⁺ calc. 279.9932, obs. 279.9934.

2.2. Synthesis of 4

Compound 2 (0.165 g, 1.15 mmol) was dissolved in 20 ml of THF. The solution was cooled to 0°C. To the cold THF solution n-BuLi (0.5 ml, 2.5 M solution) was added dropwise. The resulting solution was stirred at 0°C for 1 h. FeCl₂ (0.10 g, 0.8 mmol) was dissolved in 20 ml of THF. After refluxing for 1 h, the THF solution was cooled to 0°C and kept in an ice bath, inducing the precipitation of white precipitates (FeCl₂(THF)_{*n*}). The brown supernatant solution was removed and 5 ml of fresh THF solution were added to the precipitates. The lithium anionic solution was added via cannulation to the THF solution of FeCl₂(THF)_n. The resulting solution was refluxed overnight. After cooling, the solvent was removed and the residue was extracted with diethyl ether. The etheral solution was filtered through celite. The filtrate was concentrated and column chromatographed. After purification, orange crystalline solids were obtained in 92% (0.18 g) yield. ¹H NMR (CDCl₃): δ 7.22–7.16 (m, 10H), 4.62 (t, 1.5 Hz, 4H), 4.46 (t, 1.5 Hz, 4H) ppm. Anal. Calc. for C₂₂H₁₈Fe: C, 78.12; H, 5.36. Found: C, 77.64; H, 5.48%.

2.3. Synthesis of 5

Compound **4** (0.15 g, 0.44 mmol) and $Cr(CO)_6$ (0.10 g, 0.48 mmol) were dissolved in 12 ml of a mixed solvent of Bu₂O and THF (vol./vol. 10:1). The solution was refluxed for 3 days. After cooling to room temperature, the solvent was removed, and the residue was extracted with diethyl ether. The etheral solution was filtered through celite. The filtrate was concentrated and column chromatographed on silica gel eluting with hexane and diethyl ether (vol./vol. 20:1). After purification, orange crystalline solids were obtained in 77% (0.16 g) yield. IR (CsF): ν (CO) 1959, 1883 cm⁻¹. ¹H NMR (CDCl₃): δ 7.36–7.18 (m, 5H), 5.31–5.11 (m, 5H), 4.59 (t, 1.83 Hz, 2H), 4.36 (t, 1.83 Hz, 2H), 4.31 (t, 1.83 Hz, 4H) ppm. *Anal.* Calc. for C₂₅H₁₈CrFeO₃: C, 63.31; H, 3.83. Found: 62.66; H, 3.83%.

2.4. Synthesis of 7

Compound **5** (0.065 g, 0.14 mmol) and [(naphthalene)Mn(CO)₃]BF₄ (0.05 g, 0.14 mmol) were dissolved in 20 ml of CH₂Cl₂. The solution was refluxed for 3 h under dark. After cooling to room temperature, the solution was filtered through celite. The filtrate was added to 50 ml of diethyl ether to precipitate the product. The analytically pure red crystalline product was recrystallized from CH₃NO₂/diethyl ether. The yield was 32% (0.028 g). IR (CsF): ν (CO) 2072, 2020, 1963, 1888 cm⁻¹. ¹H NMR (CD₃NO₂): δ 6.68 (t, 6.7 Hz, 1H), 6.37 (d, 6.7 Hz, 2H), 6.29 (t, 6.7 Hz, 2H), 5.63 (m, 4H), 5.49 (m, 1H), 5.03 (br. s, 2H), 4.83 (br. s, 4H), 4.51 (br. s, 2H) ppm. FAB mass (low resolution): $M^+ - \text{Cr}(\text{CO})_3 477, \text{Cr}(\text{CO})_3^+ 136.$

2.5. Synthesis of 8

Compound **4** (0.050 g, 0.15 mmol) and [(naphthalene)Mn(CO)₃]BF₄ (0.105 g, 0.30 mmol) were dissolved in 20 ml of CH₂Cl₂. The solution was refluxed for 3 h under dark. After cooling to room temperature, the solution was filtered through celite. The filtrate was added to 50 ml of diethyl ether to precipitate the product. The analytically pure red crystalline product was recrystallized from CH₃NO₂/diethyl ether. The yield was 45% (0.053 g). IR (CsF): ν (CO) 2076, 2020 cm⁻¹. ¹H NMR (CD₃NO₂): δ 6.78 (t, 6.1 Hz, 4H), 6.51 (d, 6.1 Hz, 4H), 6.40 (t, 6.7 Hz, 2H), 5.11 (br. s, 4H), 4.83 (br. s, 4H) ppm. *Anal.* Calc. for C₂₅H₁₈B₂-F₈Mn₂O₆: C, 42.58; H, 2.30. Found: C, 42.03; H, 2.24%.

Analytical data for **9**. ¹H NMR (CDCl₃): δ 7.77–7.11 (m, 11H), 3.79–3.74 (dd, 7.1, 2.9 Hz, 1H), 3.34–3.19 (ddd, 19.8, 7.1, 3.2 Hz, 2H), 2.89–2.76 (ddd, 19.8, 2.9, 2.7 Hz, 2H) ppm. HRMS: M^+ calc. 234.1045, obs. 234.1216.

Analytical data for **10**. ¹H NMR (CDCl₃): major isomer, δ 7.65–7.12 (m, 10H), 6.94 (t, 1.2 Hz, 2H), 3.79 (t, 1.2 Hz, 2H) ppm; minor isomer, 7.65–7.12 (m, 10H), 6.65 (td, 1.9, 1.7 Hz, 1H), 3.60 (dd, 1.9, 1.0 Hz, 2H) ppm.

2.6. Synthesis of 11

Compound **10** (0.186 g, 0.85 mmol) and Mn₂(CO)₁₀ (0.432 g, 1.10 mmol) were dissolved in 30 ml of xylene. The solution was refluxed for 2 days. After cooling to room temperature, the solvent was removed, and the residue was extracted with diethyl ether. The etheral solution was filtered through celite. The filtrate was concentrated and column chromatographed on silica gel eluting with hexane. After purification, bright yellow solids were obtained in 64% (0.19 g) yield. IR (NaCl): ν (CO) 2016, 1925 cm⁻¹. ¹H NMR (CDCl₃): δ 7.54–7.26 (m, 10H), 5.67 (t, 1.8 Hz, 1H), 5.24 (d, 1.8 Hz, 2H) ppm. *Anal.* Calc. for C₂₀H₁₃MnO₃: C, 67.42; H, 3.69. Found: 67.19; H, 3.64%.

2.7. Syntheses of 12 and 13

Compound **11** (0.184 g, 0.52 mmol) and $Cr(CO)_6$ (0.114 g, 0.52 mmol) were dissolved in 12 ml of n-Bu₂O and THF (vol./vol. 10:1). The solution was refluxed for 3 days. After cooling to room temperature, the solvent was removed, and the residue was extracted with diethyl ether. The etheral solution was filtered through celite. The filtrate was concentrated and column chromatographed on silica gel eluting with a mixture solvent of hexane and ethylacetate (vol./vol. 20:1). After purification, **12** and **13** were obtained in the ratio of 60% (0.15 g) and 15% (0.05 g). When 4 equiv. of $Cr(CO)_6$ were used, **12** and **13** were obtained in the ratio of 20% and 43%.

Analytical data for **12**. IR (NaCl): ν (CO) 2024, 1968, 1938, 1890 cm⁻¹. ¹H NMR (CDCl₃): δ 7.50–7.34 (m, 5H), 5.58–5.20 (m, 8H) ppm. *Anal*. Calc. for C₂₃H₁₃CrMnO₆: C, 56.12; H, 2.66. Found: C, 55.80; H, 2.89%.

Analytical data for **13**. IR (NaCl): ν (CO) 2020, 1968, 1938, 1892 cm⁻¹. ¹H NMR (CDCl₃): δ 5.48–5.30 (m, 10H), 5.29 (s, 1H), 5.17 (d, 1.8 Hz, 2H) ppm. HRMS: M^+ calc. 627.8750, obs. 627.8770.

2.8. Syntheses of 14 and 15

Compound **10** (0.047 g, 0.21 mmol) and Fe₂(CO)₉ (0.20 g, 0.55 mmol) were dissolved in 30 ml of benzene. The solution was refluxed for 6 h. After cooling to room temperature, the solvent was removed, and the residue was extracted with diethyl ether. The etheral solution was filtered through celite. The filtrate was concentrated and column chromatographed on silica gel eluting with hexane and hexane/ethyl acetate (vol./vol. 10:1). After purification, bright yellow solids **14** and **15** were obtained in 57% (0.05 g) and 28% (0.04 g) yield, respectively.

Analytical data for **14**. IR (NaCl): ν (CO) 2032, 1962 cm⁻¹. ¹H NMR (CDCl₃): δ 7.54–7.19 (m, 10H), 6.10 (s, 2H), 3.83 (d, 11.84 Hz, 1H), 3.02 (d, 11.84 Hz, 1H) ppm. HRMS: M^+ – CO calc. 330.0343, obs. 330.0211.

Analytical data for **15**. IR (NaCl): ν (CO) 1978, 1773 cm⁻¹. ¹H NMR (CDCl₃): δ 7.52–7.24 (m, 20H, Ph), 5.60 (d, 1.9 Hz, 2H), 4.77 (d, 1.9 Hz, 4H) ppm. *Anal*. Calc. for C₃₈H₂₆Fe₂O₄: C, 69.33; H, 3.98. Found: C, 69.58; H, 4.01%.

2.9. Synthesis of 16

Compound **10** (1.0 g, 4.6 mmol) was dissolved in 30 ml of THF. n-BuLi (2.0 ml, 2.5 M solution) was added to the THF solution at 0°C. After stirring for 1 h at 0°C, FeCl₂ (0.32 g, 2.5 mmol) was added. The resulting solution was refluxed for 12 h. After cooling to room temperature, the solvent was removed, and the residue was extracted with diethyl ether. The etheral solution was filtered through celite. The filtrate was concentrated and column chromatographed on silica gel eluting with hexane. After purification, yellow solids (1.22 g) were obtained quantitatively. ¹H NMR (CDCl₃): δ 7.20

(br. s, 20H), 4.62 (t, 3.75 Hz, 2H), 4.45 (d, 3.75 Hz, 4H) ppm. *Anal.* Calc. for $C_{34}H_{26}Fe: C, 83.27$; H, 5.34. Found: 82.92; H, 5.26%.

2.10. Synthesis of 17

Compound **16** (0.10 g, 0.20 mmol) and $Cr(CO)_6$ (1.0 g, 4.5 mmol) were dissolved in a mixed solvent of n-Bu₂O (50 ml) and THF (10 ml). The solution was refluxed for 3 days. During refluxing, orange solids were precipitated. The solution was cooled to room temperature and the precipitates were filtered off. The precipitates were washed with diethyl ether (10 ml×3) and then washed with CH₂Cl₂ (5 ml×2). The purified product was obtained by recrystallization from acetone/hexane. The yield was 78% (0.14 g). ¹H NMR (d₆-acetone): δ 5.85–5.45 (m, 22H), 5.00 (d, 1.4 Hz, 4H) ppm. *Anal.* Calc. for C₄₆H₂₆Cr₄FeO₁₂: C, 53.41; H, 2.53. Found: 54.01; H, 2.28%.

2.11. X-ray structure determination of 8

A crystal of 8 having approximate dimensions of $0.50 \times 0.20 \times 0.10$ mm was mounted on a glass fiber. Preliminary examination and data collection were performed with Mo K α radiation ($\lambda = 0.71073$ Å) on an Enraf-Nonius CAD4 computer controlled kappa axis diffractometer equipped with a graphite crystal monochromator. Cell constants and an orientation matrix for data collection were obtained from least-squares refinement, using the setting angle of 25 reflections in the range $2.03 < \theta < 22.48^{\circ}$, measured by the computer controlled diagonal slit method of centering. The data were collected at room temperature using the omega scan technique. A total of 1733 unique reflections was collected. Lorentz and polarization corrections were applied to the data. No absorption correction was applied to the data. The structure was solved by direct method using SHELXS-86 [20] and refined by full-matrix least-squares with SHELXL-93 [21]. All non-hydrogen atoms were refined anisotropically; hydrogen atoms were refined isotropically using a riding model with 1.2 times the equivalent isotropic temperature factors of the atoms to which they are attached. The anion tetrafluoroborate is disordered. Crystal data, details of the data collection, and refinement parameters for 8 are listed in Table 1. Final atomic positional parameters for the non-hydrogen atoms are shown in Table 2, and selected bond distances and angles are given in Table 3; see also Section 4.

2.12. X-ray structure determination of 12

A single crystal of 12 was a clear yellow prism with natural faces, but somewhat small, so intensities were mostly low. Data collection was carried out with a Siemens P4 singlecrystal diffractometer controlled by XSCANS version 2.1 software [22]. Omega scans were used for data collection, at variable speeds from 10 to 60° per min. Three standard reflections were measured after every 97 reflections; they

Table 1Crystal and refinement data for 8 and 12

	8	12
Molecular formula	C ₂₈ H ₁₈ B ₂ F ₈ Mn ₂ O ₆	C ₂₃ H ₁₃ CrMnO ₆
Formula weight	743.76	492.27
Crystal system	monoclinic	monoclinic
Space group	$P2_1/n$	$P2_1/c$
a (Å)	7.4732(14)	16.164(3)
b (Å)	13.852(2)	10.601(2)
<i>c</i> (Å)	14.813(4)	12.424(3)
α (°)	90	90
β (°)	101.47(2)	103.64(2)
γ (°)	90	90
$V(Å^3)$	1502.7(6)	2068.8(7)
Ζ	4	4
$D_{\rm calc} ({\rm Mg}{\rm m}^{-1})$	1.644	1.581
Crystal size (mm)	$0.50 \times 0.20 \times 0.10$	$0.24 \times 0.26 \times 0.47$
λ (Å)	0.71073 (Mo Kα)	0.71073 (Mo Kα)
Total no. unique reflections	1997	3646
2θ Range (°)	4-50	5-50
No. parameters	214	280
R	0.0762	0.0584
wR^2	0.2087	0.1409
Goodness of fit	1.082	0.905

Table 2

Atomic coordinates ($\times 10^4)$ and equivalent isotropic displacement parameters ($\mathring{A}^2 \times 10^3)$ for ${\bf 8}$

_	x	у	z	U_{eq}
Fe	0	5000	5000	39(1)
Mn	2337(1)	1698(1)	3898(1)	48(1)
C(1)	1497(9)	3809(5)	4864(4)	46(1)
C(2)	1150(10)	3869(5)	5776(4)	50(2)
C(3)	1888(11)	4737(6)	6172(5)	60(2)
C(4)	2687(9)	5218(6)	5543(5)	57(2)
C(5)	2484(9)	4663(5)	4728(5)	54(2)
C(6)	903(9)	3059(5)	4187(5)	45(1)
C(7)	-49(9)	2230(5)	4404(5)	55(2)
C(8)	-597(11)	1516(6)	3722(7)	74(2)
C(9)	-126(12)	1567(6)	2883(6)	73(2)
C(10)	816(13)	2373(6)	2672(5)	71(2)
C(11)	1363(10)	3093(5)	3297(4)	51(2)
C(01)	3703(14)	1133(7)	3186(6)	78(3)
C(02)	2625(12)	615(6)	4613(7)	70(2)
C(03)	4353(12)	2209(6)	4618(6)	70(2)
O(01)	4577(13)	758(7)	2740(6)	136(4)
O(02)	2827(11)	-45(5)	5046(6)	113(3)
O(03)	5610(12)	2536(6)	5075(6)	121(3)
В	10191(17)	1370(7)	7055(7)	74(3)
F(1)	9294(9)	669(4)	7463(5)	108(2)
F(2)	9006(11)	1964(6)	6555(5)	124(3)
F(3)	11097(14)	1881(6)	7782(6)	155(3)
F(4)	11275(15)	933(6)	6614(7)	187(5)

 $U_{\rm eq}$ is defined as one third of the trace of the orthogonalized U_{ij} tensor.

showed a 2.4% decline over the course of data collection, and corrections were made for their variation. Profile fitting was used for the reduction of the data and an empirical absorption correction was applied, based on Ψ -scans. The structure was

Table 3	
Selected bond lengths (Å) a	and bond angles (°) for 8

Fe–C(1)	2.025(6)	Fe–C(3)	2.040(7)
Mn-C(6)	2.251(6)	Mn-C(8)	2.170(8)
Mn-C(03)	1.808(9)	C(01)-O(01)	1.141(10)
C(1)–Fe–C(2)	41.2(2)	C(1)-Fe-C(4)	68.8(3)
C(1)-C(2)-C(3)	108.4(6)	C(2)-C(1)-C(5)	106.4(6)
C(7)-C(6)-C(11)	117.3(6)	C(8)-C(9)-C(10)	118.9(8)
Mn-C(02)-O(02)	178.9(8)	C(01)-Mn-C(03)	90.7(4)

determined by direct methods and refined initially by use of programs in the SHELXTL PC version 5.1 package [22], which were also used for all figures. All 13 hydrogen atoms appeared in a difference map, and each was introduced in an ideal position, riding on the atom to which it is bonded; each was refined with a isotropic temperature factor 20% greater than that of the ridden atom. All other atoms were refined with anisotropic thermal parameters. Since chromium and manganese differ by only one electron, the atoms were interchanged as a check of their identification; the discrepancy values were poorer and the structure became less regular. Final refinement on F^2 was carried out using SHELXL 93 [21]. Crystal data, details of the data collection, and refinement parameters for 12 are listed in Table 1. Final atomic positional parameters for the non-hydrogen atoms are shown in Table 4, and selected bond distances and angles are given in Table 5; see also Section 4.

3. Results and discussion

One of the general synthetic strategies for the synthesis of cyclopentadienes is the derivatization of cyclopentenones. To synthesize the appropriate cyclopentadienyl ligand, we utilized the high-yield synthesis of cyclopentenone by the intermolecular Pauson–Khand reaction between phenylacetylene and ethylene in the presence of DMSO as a promoter [23]. After reaction, we could isolate the 1-phenylcyclopentenone in 70% yield based on (PhC=CH)Co₂(CO)₆. After reduction and dehydration, **2** was obtained in 64% yield (Eq. (1)).

$$H \xrightarrow{1) \operatorname{Co}_2(\operatorname{CO})_8, \operatorname{n-hex}}_{2) \operatorname{C}_2\operatorname{H}_4(30 \operatorname{atm})} \xrightarrow{O}_{Ph} Ph$$

$$1$$

$$1) \operatorname{NaBH}_4, \operatorname{CeCl}_3, \operatorname{MeOH}}_{2) \operatorname{MgSO}_4, \operatorname{n-hex}, \uparrow \downarrow} Ph \xrightarrow{} Ph \xrightarrow{} + \operatorname{isomers} (1)$$

When 2 was refluxed with $Mn_2(CO)_{10}$ in xylene, 3 was obtained in 50% yield (Eq. (2)).

Table 4 Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\mathring{A}^2 \times 10^3$) for **12**

	x	у	z	$U_{ m eq}$
Mn(1)	2272(1)	2159(1)	5150(1)	58(1)
Cr(1)	3629(1)	-2499(1)	5261(1)	60(1)
C(1)	3293(3)	-452(5)	5050(5)	59(2)
C(2)	3867(3)	-648(5)	6111(5)	62(2)
C(3)	4646(4)	-1237(6)	6179(6)	79(2)
C(4)	4873(4)	-1689(7)	5204(8)	92(2)
C(5)	4322(4)	-1476(7)	4169(6)	82(2)
C(6)	3533(4)	-885(6)	4126(5)	67(2)
C(7)	2466(3)	179(5)	4988(4)	54(1)
C(8)	1902(3)	641(5)	4009(4)	60(2)
C(9)	1177(4)	1135(5)	4282(5)	67(2)
C(10)	1254(3)	969(5)	5434(4)	55(1)
C(11)	2051(3)	392(5)	5858(5)	57(2)
C(12)	608(3)	1264(6)	6040(5)	67(2)
C(13)	-65(4)	2075(7)	5624(6)	87(2)
C(14)	-668(5)	2361(8)	6193(9)	105(3)
C(15)	-626(4)	1824(9)	7202(9)	101(3)
C(16)	28(4)	1008(7)	7643(6)	88(2)
C(17)	638(4)	734(7)	7073(6)	76(2)
C(18)	2988(4)	-3410(6)	4120(5)	77(2)
O(1)	2563(4)	-3949(5)	3392(4)	123(2)
C(19)	4186(5)	-3942(7)	5848(7)	107(3)
O(2)	4543(4)	-4836(6)	6216(6)	160(3)
C(20)	2821(5)	-2847(7)	6028(6)	81(2)
O(3)	2303(4)	-3080(7)	6485(5)	133(2)
C(21)	3191(5)	2460(7)	6205(6)	110(3)
O(4)	3808(5)	2632(7)	6871(5)	199(4)
C(22)	2744(5)	2953(7)	4180(6)	85(2)
O(5)	3075(5)	3436(6)	3566(5)	138(2)
C(23)	1762(5)	3540(8)	5440(8)	116(3)
O(6)	1420(5)	4424(6)	5619(7)	182(4)

 $U_{\rm eq}$ is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Table 5

Selected bond lengths (Å) and bond angles (°) for 12

$ \begin{array}{c} Mn(1)-C(21) \\ C(1)-C(2) \\ C(1)-C(7) \\ Cr(1)-C(4) \\ Cr(1)-C(4) \\ Cr(1) \\ \end{array} $	1.763(8) 1.437(7) 1.480(8) 2.204(6) 1.151(7)	C(21)-O(4) C(1)-C(6) Cr(1)-C(1) Cr(1)-C(18) Cr(10)-C(12)	1.150(8) 1.375(8) 2.237(6) 1.823(7) 1.458(8)
C(18)-O(1) $C(23)-Mn(1)-C(21)$ $C(8)-C(7)-C(11)$ $Mn(1)-C(23)-O(6)$ $C(1)-Cr(1)-C(4)$	92.9(4) 105.9(5) 178.8(8) 79.4(2)	C(10)-C(12) C(9)-C(10)-C(11) C(8)-C(7)-C(1) Cr(1)-C(19)-O(2) C(2)-C(1)-C(6)	106.6(5) 126.1(5) 179.2(7) 118.0(5)
-			



Several years ago, Rausch and co-workers [16] reported the preparation of **3** by the reaction of phenylcyclopentadienylthallium and $Mn(CO)_5Br$.

One of the ways to prepare heteronuclear complexes is to use free cyclopentadiene or phenyl groups(s). Compound **3** has a phenyl substituent on the cyclopentadienyl ring. Thus treatment of **3** with $Cr(CO)_3(NH_3)_3$ gave the diarene Cr– Mn bimetallic compound [24]. In the same way, treatment of **3** with (naphthalene) $Mn(CO)_3^+$ led to a dimanganese complex (Eq. (3)).

$$\mathbf{3} + \underbrace{\bigwedge_{Mn^{+} (CO)_{3}}^{(CO)_{3}}}_{Mn^{+}} \underbrace{\xrightarrow_{CH_{2}Cl_{2}, \uparrow\downarrow}}_{Mn} \underbrace{\bigwedge_{Mn^{+} (CO)_{3}}^{(CO)_{3}}}_{Mn} (3)$$

unstable

However, the dimanganese compound was not stable enough to characterize completely. While taking ¹H NMR, the dimanganese compound decomposed. The carbonyl stretching frequencies in nitromethane appeared at 2072, 2024 and 1946 cm⁻¹. We could assign the peaks at 2072 and 2024 cm⁻¹ as arising from $(\eta^6-C_6H_5)Mn(CO)_3^+$ and at 2024 and 1946 cm⁻¹ as arising from $(\eta^5-C_5H_4)Mn(CO)_3$.

Treatment of **2** with n-BuLi and then with $FeCl_2$ in refluxing THF gave **4** in 92% yield (Eq. (4)).

$$2 + FeCl_2 \xrightarrow{\text{THF}, \uparrow\downarrow} Fe \xrightarrow{Fe} (4)$$

4

It was reported [25] that **4** could be prepared in 20% yield by the reaction of ferrocene with phenyldiazonium salt. Compound **4** was reacted further with 1 equiv. $Cr(CO)_6$. After workup, we could isolate **5** in 77%. When excess $Cr(CO)_6$ was used, **6** was obtained as a sole product in 83% (Eq. (5)).



Compound **6** has been previously prepared by an alternate route [26]. When **5** was reacted with (naphthalene)- $Mn(CO)_3^+$ [18], we could isolate the cationic complex **7** in 32% yield (Eq. (6)).



If we used other methods (e.g. Fischer-Hafner method [27] or silver method [28]) to coordinate $Mn(CO)_3^+$ to the free phenyl ring, the $Cr(CO)_3$ moiety could not tolerate the reaction conditions. The $Mn(CO)_3^+$ transfer by $(naphthalene)Mn(CO)_3^+$ was so mild that we could prepare 7. Compound 7 contains three different metals, e.g. Cr, Mn and Fe.

Treatment of 4 with excess (naphthalene) $Mn(CO)_3^+$ in CH₂Cl₂ yielded the dicationic Fe-Mn₂ complex 8 in 45% yield (Eq. (7)).



Single crystals of 8 suitable for X-ray studies were grown by the diffusion of diethyl ether into a nitromethane solution of 8. The molecular geometry and labeling scheme for 8 is shown in Fig. 1, and selected bond distances and angles are given in Table 3. The crystal structure of 8 was quite different from that of 6 [26]. While 6 adopts an eclipsed conformation with the phenyl groups located in the same direction, 8 adopts a typical 1,3'-orientation which minimizes steric repulsions. The typical 1,3'-orientation was explained on the ground of minimization of steric repulsion or an efficient packing within the crystal [29]. The manganese atom is located 1.678 Å below the plane of the phenyl ring. The iron atom is located 1.640 Å below the plane of the cyclopentadienyl ring. The torsion angle between the cyclopentadienyl ring and phenyl ring is 1°.

A mixture of isomers of diphenylcyclopentadiene (10) is readily prepared from the Pauson-Khand reaction followed by reduction and dehydration (Eq. (8)) [5].

$$Ph \longrightarrow H + Ph \land \xrightarrow{Co_2(CO)_8} Ph \land \xrightarrow{O} Ph$$

$$\xrightarrow{1) \text{ NaBH}_4, \text{CeCl}_3, \text{MeOH}}_{2) \text{ MgSO}_4, \text{n-hex}, \uparrow\downarrow} \xrightarrow{Ph} \xrightarrow{Ph} + \text{ isomers}$$
(8)

When 10 was refluxed with $Mn_2(CO)_{10}$ in xylene, 11 was obtained in 64% yield (Eq. (9)).

$$10 + Mn_2(CO)_{10} \xrightarrow{xylene, \uparrow\downarrow} Ph \xrightarrow{Ph - Ph}_{Mn} (9)$$

When we used $Mn(CO)_3(py)_2Br$ [30,31] as an Mn(CO)₃ source, **11** was obtained in 30% yield. Compound



Fig. 1. Molecular structure of compound 8, with the atomic labeling scheme.

11 has two free phenyl rings which can be coordinated to other organometallic moieties. Thus, when 11 was reacted further with $Cr(CO)_6$, 12 and 13 were obtained (Eq. (10)).

$$11 + Cr(CO)_6$$



13 (10)

When 1.3 equiv. $Cr(CO)_6$ was used, 12 and 13 were obtained in the ratio of 4:1 with a total yield of 75%. Compounds 12 and 13 were easily separated by flash column chromatography eluting with hexane and ethylacetate (vol./ vol. 20:1). When $Cr(CO)_3(CH_3CN)_3$ was used as the $Cr(CO)_3$ source, the yield was rather poor. Single crystals of 12 suitable for X-ray studies were grown by diffusion of hexane into a methylene chloride solution of 12. The molecular geometry and labeling scheme for 12 are shown in Fig. 2, and selected bond distances and angles are given in Table 5.



Fig. 2. Molecular structure of compound 12, with the atomic labeling scheme.

The two metals (Cr and Mn) are on the opposite faces of a bridging hydrocarbon in *anti* arrangement as expected due to steric repulsion. The Mn atom in **12** has the usual piano-stool coordination characteristic of monocyclopentadienyl complexes [32]. The cyclopentadienyl ring (C7–C11) is planar with a mean deviation of 0.005 Å. The Mn atom is located 1.773 Å below the plane of the cyclopentadienyl ring. The phenyl ring (C1–C6) is planar with a mean deviation of 0.008 Å. The Cr atom is located 1.714 Å below the plane of the phenyl ring. The dihedral angle between the planes C1–C6 and C7–C11 is 14.6°. The C–O bond distances in the carbonyl groups are rather insensitive to the metal moieties, and the average C–O distance is 1.146 Å.

Treatment of **10** with $Fe_2(CO)_9$ in refluxing benzene gave a cyclopentadiene compound **14** (57%) and a cyclopentadienyl dimeric compound **15** (28%) (Eq. (11)).



This reaction is somewhat different from the reaction of dialkyl-1,3-cyclopentadienes with Fe(CO)₅. In the reaction between dialkyl-1,3-cyclopentadienes with Fe(CO)₅, only substituted cyclopentadienyl dicarbonyl dimers are obtained [33]. However, Rausch and co-workers [34] reported the preparation of pentabenzylcyclopentadiene, C₅Bz₅H. The reaction between C_5Bz_5H and $Fe(CO)_5$ in refluxing toluene led to the formation of $[(\eta^5-C_5Bz_5)Fe(CO)_2]_2$ (8%) and $(\eta^4$ -C₅Bz₅H)Fe(CO)₃ (25%). Their results look almost the same as ours, but the yields and ratios are quite different from ours. In fact, at first we expected only a dimeric compound with bridging carbonyls. It is anticipated that the exo hydrogen in 14 can be easily removed [35] and that 15 will be easily cleaved by reduction [36]. Thus, we expect that 14 and 15 can be used as versatile precursors for the syntheses of acyclic compounds.

Refluxing of the lithium salt of 1,3-diphenylcyclopentadienide with FeCl_2 in THF afforded **16** in an almost quantitative yield (Eq. (12)).

10 1) n-BuLi, THF
2) FeCl₂, THF,
$$\uparrow\downarrow$$
 Ph Ph Ph
Fe (12)
Ph-Ph
Fe (12)

16

Recently, the synthesis and molecular structure of **16** has been reported by other groups [37]. They obtained **16** in less than 60% yield. When **16** was refluxed with excess $Cr(CO)_6$, the formation of several compounds was observed, which

contained various ratios of chromium, e.g., Fe/Cr, Fe/Cr₂, Fe/Cr₃ and Fe/Cr₄ (Eq. (13)).

(13)

17

Fortunately, the Fe/Cr₄ **17** has a very different solubility from other Fe/Cr_n (n = 1, 2, 3) compounds. While others are soluble in CH₂Cl₂, **17** is insoluble in CH₂Cl₂ and slightly soluble in acetone. As a result, after washing the reaction products with CH₂Cl₂, **17** was obtained in 78% yield. Compound **17** contains five metals in a single molecule.

We have demonstrated a route for diarene-bridged heterobi- and polymetallic complexes by which chromium, manganese and iron metals can be rationally introduced. We have crystallographically characterized two of these complexes. Further research related to the physical properties of polymetallic compounds is in progress.

4. Supplementary material

Tables of complete bond distances and bond angles, anisotropic thermal parameters, and hydrogen atom coordinates for complexes 8 and 12 are available from the authors.

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